PROPERTIES AND REACTIONS EXHIBITED BY VITRINOID MACERALS
FROM BITUMINOUS COALS

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The commercially important bituminous coals are composed in large part of vitrinitic substances. This fact coupled with what has been a somewhat vaguely defined association of these substances with the coking characteristics of coal places a premium value on any specific information concerning the nature and properties of these organic coal components. The data presented and discussed in the following pages represents a portion of the results obtained in the course of a program of research focused upon these materials.

The first phase of the investigation was initiated in 1952 and this dealt with the problem of developing petrographic descriptions of coal seams which would serve to predict the coking properties of any given coal. Preliminary studies brought out the fact that coal is made up of a complex of materials or entities, each possessing different optical properties, and presumably possessing differing chemical characteristics and carbonizing properties. These preliminary studies also demonstrated that the descriptive systems heretofore used were inadequate to allow differentiation of the coal macerals that were important in determining reacting properties. As a starting point, the most detailed of the existing descriptive systems, the one that had evolved out of the work of Stopes (1935) was used to describe a number of coal seams occurring in a single mining area in Kentucky.

The coal seams of this area are all of High Volatile "A" rank, and were very similar in their proximate and ultimate analyses, but great differences were noted when they were carbonized to produce metallurgical coke. This presented the opportunity to determine whether these differences in coking ability could be related to the petrography of the coal. The petrographic evaluations showed that the seams varied in entity composition. In addition, the investigation revealed that the seams varied in that they were differentially banded, that is, each coal seam was made up of many layers of differing composition. These layers of differing composition were called the petrographic divisions of the coal seam. Figure 1 presents a typical petrographic analysis. Note that within this seam there are 22 layers or petrographic divisions each differing in composition from the ones immediately adjacent to it.

From the petrographic data amassed on these seams it became apparent that if sufficient material could be obtained from some of these distinct bands occurring in the subject coals, test samples would be available that ranged in the major component composition from 38 % to 92% vitrinite, 1% to 35% exinite, 5% to 40% micrinite and from essentially none to about 14% fusinite. This material could then be carbonized and subjected to the tests used to evaluate metallurgical coke in order to demonstrate the effect of the petrographic composition of the coals. Several hundred pounds of each of 19 narrow coal bands were hand mined from three coal seams. This material was cut into two parts: one for a petrographic check, and the other was coked in duplicate in a 30 pound test oven and subjected to drop-shatter, tumbler and micro-strength evaluations. The results of these investigations have already been reported (Spackman, Brisse, Berry, 1957). In brief, the conclusions were as follows:
1. That in general the material designated fusinite was detrimental to coke strength if present in large particle size because it served as a locus of fracture points.

2. That the material micrinite was beneficial to coke strength up to a certain concentration. This action was likened to a concrete mixture. Pure cement will not make a strong product (cement = vitrinite); when aggregate is added to the cement - water mixture up to a certain limit, a very strong product results (aggregate = micrinite). Therefore there is, for concrete, an optimum mixture for greatest product strength, likewise these tests indicated that there was also an optimum maceral ratio for maximum coke strength. For the coals initially studied this ratio is on the order of 3 parts vitrinite to one part micrinite.

3. That the material exinite contributed to the bonding capacity of certain coal blends and when present in concentrations of over 10%, materially enhanced the strength of the coke.

4. That the material vitrinite is the prime factor controlling the carbonizing properties of the coals tested. This is in part due to its great predominance in the subject coals. No entire seam investigated contained less than 50% of this material and one had greater than 80% vitrinite. Secondly, this material is one of the substances of the coal that produces its fluid characteristics when heated. Figure 2 presents the expressed relationship between the vitrinite content and the coke strength (reproduced from Spackman, Brisse and Berry, 1957). Notice that there is an optimum amount of this material associated with maximum coke strength and that an excess or deficiency of the material results in a loss of coke strength.

With this correlation in hand it was decided to test further the validity of the inferred relationship by coking samples on a larger scale (500# test oven). If the curve was valid each samples' vitrinite content would cause it to fall on the correlation curve. Figure 3 presents the results of these experiments. Note that four of the five points fall where expected, but the fifth, a known poor coking coal, fell completely off the supposed correlation curve. Re-examination of this fifth sample brought out a very curious fact: the material classed as vitrinite in this coal contained a variety of materials with differing optical properties but under the descriptive system used there was no choice other than to classify them as vitrinite. Re-evaluation of the other four seams showed that this was true to a much lesser degree. Sample 5 was found to contain between 15% and 20% of materials that differed from the typical "vitrinite" which predominated in the other four samples. For the time being the more abundant material was called vitrinite, and when sample 5 was re-analyzed counting only this material as "vitrinite", the point moved to the predicted position as shown on the other graphs in Figure 3.

It would appear then that:
1. The maceral terms as proposed by Stopes do not, in fact, describe the basic entities of coal, rather they include a group of genetically related materials that in actuality differ in optical, physical and chemical properties.

2. Recognizing the variability within any one of Stopes' "macerals" it was suggested that these terms be elevated to a maceral group status because there was a value in retaining the genetic aspects of the classification. This would allow the description of the entities occurring in the group and their designation as macerals (see Spackman, 1958).

3. To facilitate this the following changes are suggested: Stopes' terms have achieved world wide recognition in describing coal materials so in order to avoid confusion, it is suggested that these descriptive names be retained but the suffix changed to "oid" to designate that these represent a group of materials, and, that as the macerals are described, they be named appropriately and use the ending "inite".

For present purposes the macerals comprising any one group are designated by type number until more complete data has been amassed. Table 1 presents the classification as it is presently used.

Table 1

Maceral Groups	Vitrinoids									Micrinoids		Fusinoids		Resinoids			Exinoids		
	Type I	Type II	Type III	Type IV	Type V	Type VI	Type VII	Type VIII	Type IX	Type I	Type II	Type I	Type II	Type I	Type II	Type III	Type I	Type II	Type III

·Utilizing this classification system, the next phase of research opened with the sampling of coals of all ranks from widely separated geographical areas. Coals were collected from Utah, Illinois, Pennsylvania, Ohio, West Virginia, Kentucky and Alabama. All of these coals were examined using normal petrographic methods and their entities classified on the basis of their optical properties. This completed, the next step was to be sure that the entities classified by optical means were indeed different in their reactive properties.

To facilitate this, and since the primary interest at the time was the ability to predict any coal's coking potential, a research instrument was assembled to evaluate the thermal properties of the entities. A Leitz 1000° heating stage, a research microscope and a temperature control unit comprise the basic components of the assembly. This apparatus is shown in Figure 4. This heating stage can be brought, at any rate of heat, to any temperature between 0 and 1000° Centigrade. It is so built that a sample can be viewed in transmitted or reflected light while being brought through its heating cycle. A nitrogen atmosphere is maintained in the furnace to stop oxidation of the subject material. All reactions can be biewed as they occur, and to facilitate the recording of the data a time lapse motion picture camera is included in the system. This allows the recording by color motion pictures of the reactions of the various entities as they take place. Figure 5 presents a picture of the control panel associated with this heating stage microscope. The incorporation of a program controller in the system allows the selection of any rate of heat from 3° to 15°C./minute, by setting the desired rate on the upper left timer control. If a period of soaking at any temperature between 100° and 900°C. is desired, the controller can be set to cut out at that temperature, the soak timer (directly below the aforementioned rate controller) can be set to any period of time and will cause the main controller to maintain the desired temperature. At the close of the soaking period the timer will throw the control to the right hand rate controller which will pick up the original rate of heat or any other desired rate. The camera control (left lower center) allows camera speeds of 1 frame every 5 seconds to 8 frames per second. A secondary piece of equipment allows camera speeds up to 32 frames per second. Figure 6 illustrates the type data that can be obtained by microcinephotography. The sequence on the left shows a mass of exinoid material just at its melting point, the next frame shows it in a partially fluid state, the third in a totally fluid state and the fourth shows its residue. The sequence on the right shows the melting and volatilization of one of the resinoids. Note that it is almost completely volatilized in the last frame. After preliminary investigations on several of the important coal macerals to ascertain that they were different in their reacting properties, it was decided to work first with the group of materials occurring most abundantly in the coal. These were the vitrinoids. The suite of coals were thoroughly studied microscopically and the nine most prominent vitrinoids were isolated for detailed property analysis.

The first series of tests involved the heating of specific vitrinoid types at a heating rate of 3°C/min. which is roughly equivalent to the rate of heat used in a commercial coke oven. Figure 7 presents the results of this study. All of the data presented are based on at least five runs in which reproducible results were obtained. Note that the entities studied can be grouped into three categories: Non-Plastic, Semi-Plastic, and Plastic types. The non-plastic vitrinoids, Types I and II, are predominant in occurrence in High Volatile C and B coals and for all intents and purposes are inert at this rate of heat. The semi-plastic vitrinoid, Type IX, is common in occurrence in the low volatile coals but in general its percent occurrence

is low. The plastic materials Types III, IV, V, VI, VII, and VIII are found in
varying amounts throughout the bituminous coal range. Based on the coals studied to
date, it appears that these nine vitrinoid types appear in the range of bituminous
coals as shown in Table 2.

Table 2

Influence of Vitrinoid Type on Rank Designation of Bright Coals

| Vitrinoid Composition of Typical Bituminous Coals | | | Resultant Rank |
Predominant Type	Major Types	Minor Types	Designation
I	II	III and IV	High Volatile C
II	I and III	IV, V and VI	High Volatile B
IV	III and V	II, VI and VII	High Volatile A
VII	IV and VIII	III, IV, V, IX	Medium Volatile
VIII	VI and VII	V and IX	Low Volatile

Although all of the vitrinoid types described in Figure 7 exhibit some difference
in the manner in which they respond to this heating program, similarities are evident
in the case of the plastic varieties. An attempt has been made to emphasize this
fact by separating obviously dissimilar materials with horizontal lines.

Figure 8 presents data on an identical study using a heating rate of $12^{\circ}C$ per
minute, the object being to determine the manner in which each vitrinoid reacts
under another set of conditions. One of the most striking differences apparent is
that there are no longer vitrinoids which fail to show fluidity when this accelerated
heating rate is used. Notice that the capacity to fuse with similar particles is
enhanced in every case, also that the parallel lines delineating vitrinoids of similar
properties have shifted.

From these studies involving only a change in rate of heat, two major conclusions
can be drawn: 1. that the optically distinct vitrinoid types do possess differing
thermal properties and can be expected to react differently in certain industrial
processes; 2. that an increase in heating ratio elicits a variety of reactions from
the vitrinoids investigated.

The next series of tests on these vitrinoids were designed to record the differ-
ences, if any, in the reactions exhibited when the entities were subjected to shock
heating at 600 and $800^{\circ}C$.

Figure 9 illustrates the extremes in the recorded reactions of this study. In
these tests a chip of pure vitrinoid material was photographed before and after
exposure to shock heating in a top and side view. The tests shown in Figure 9 illus-
trate two vitrinoids which exhibited extremes in behavior. One of them, Type II,
actually volatilizes with such explosiveness that a loss in volume over that of the
original material results. The other material, Type VII, shows a strong swelling
to several times the size of the original material. Figure 10 illustrates some of
the results obtained in these tests. Note that Type II, when shock heated at $600^{\circ}C$.
shows little change in mass; however when shock heated at $800^{\circ}C$. a large portion of
the material volatilizes leaving a mass smaller in size than that of the original
material. Type III shows an increase in mass at 600° and an even greater expansion
at 800°. Type IV displays a strong increase in mass at 600° shock but when exposed
to temperatures of 800° the material expands strongly but has a period of contraction
before solidification. This is also true of Types VII and VIII. Type VII shows a
massive increase in volume when shocked at 600°, this is especially interesting because

coals that are associated with oven pressure problems in the metallurgical coke industry are generally rich in this vitrinoid type. When shocked at 800° Type VII displayed less expansion, perhaps indicating that when dealing with a strongly swelling coal a faster rate of heat will lessen the potential pressure dangers. Type VIII exhibits a behavior pattern similar to Type VII, however, this material swells to a much lesser degree.

Conclusions to be drawn from this test series are, again, that the subject vitrinoid types vary in their reactions and that for certain applications the desired reaction can be enhanced by a greater rate of heat.

The curve previously presented as Figure 2 which related one of the vitrinoids to coke strength showed that the presence of too much or too little of this material would cause a loss in strength. It was also noted that a ratio between this vitrinoid and the micrinoids of approximately 3 to 1 produced the strongest coke. The question then arose as to what amount of material each of the vitrinoid types could assimilate into a coke mass, and what the affect of such an assimilation would be on the strength of the resultant coke.

A series of small tests were performed using pure vitrinoid types and varying amounts of an inorganic inert material. Enough of these pure substances were picked out, with microscopic control, to allow the running of duplicate tests on each of the vitrinoid types using the following proportions (Table 3).

Table 3

Composition of Test Blends

Percent Pure Vitrinoid Type	Percent Inorganic Inert
100	0
90	10
80	20
70	30
60	40
50	50
40	60
30	70
20	80
10	90

The inert substance used was hydrated alumina and the tests consisted of coking the pure and diluted vitrinoid types in small crucibles, in an electric muffle furnace. The evaluation for strength was done on a microhardness tester.

The experimental results on the tests performed on vitrinoid Type II are presented in Figures 11, 12 and 13. Figure 11 consists of photographs of the actual coke buttons produced in the study and the unassimilated inert material. When the pure vitrinoid was coked, violent eruptions of fluid coal took place and in several cases the material produced minor explosions. This continued until 30% inert material was mixed in (refer to photographs). Note also that it is not until after 40% of inert material has been added that any unagglomerated residue appears. Notice also that the apparent stability of the coke mass improves until the amount of inerts added becomes too great to be assimilated. Figure 12 presents cross sections of the coke buttons showing the apparent effect on the coke structure of inert addition. Notice the effect of the violent reaction of this pure vitrinoid on its internal structure and how the structure stabilizes with the addition of inert material. With 80% of inert material in the mix a stable-appearing structure is still in evidence. Figure 13 presents data on the yield of coke of a particular strength. Notice that not until greater than 40% inert

material has been added does the strength drop below that of the pure maceral, in fact
at 40% dilution a slight rise in strength is noted.

The test results of vitrinoid Type III are presented in Figures 14, 15 and 16.
The coke buttons shown in Figure 14 show that this material can assimilate up to
40% of inerts without loss of the stabilizing effect. In Figure 15 the button cross-
sections show this stabilizing effect to a much greater degree than in the case of
the results obtained by blending Type II material and Figure 16 presents a set of
data which contrast markedly to those presented in Figure 13. Note that greater
than 50% inerts were added before the coke strength dropped below that of the pure
Type III material and also that there is an impressive gain in strength at the 30%
dilution level.

Figures 17, 18 and 19 represent the accumulated data on Type IV. Figure 17 again
points out the stabilizing effect of the addition of inert material. Note here that
the 50% dilution level has been reached before any unbonded inert material becomes
evident. Figure 18 substantiates the points brought out by the previous figure and
illustrates the fact that this inert additive tends to stop the fissuring apparent
in the blends high in Type IV. Figure 19 presents the strength-yield curve for this
type. Note that the inert dilution approaches 60% before the strength drops below
that of the pure maceral and there is a sizeable strength increase over a rather
large range exhibited by this maceral.

The testing of Type VII brought out several interesting points on the expansion
properties. This is especially informative because, as was mentioned before, coals
that present problems to the coke oven operator in the form of sticking charges and
unsafe pressure on the oven walls often contain large portions of vitrinoid Type VII
in their composition. Figure 20, the coke button photographs, illustrate this swell-
ing property. Note that in the picture of the pure maceral the button is the largest
and as the inert percentage becomes greater the button size decreases and generally
stabilizes in size at about 50% dilution. The fact that this material has the ability
of incorporating greater than 50% inert material into the mass is also evident.
Figure 21 makes evident one of the factors responsible for this swelling property.
Note that in the button cross-section of the 100% Type VII there is a very large
center vacuole. This vacuole was made by entrapped gases in the center of the button
which were apparently unable to force their way through the viscous surrounding
material. These gases then caused the mass to swell and with no exit route the
gases in the vacuole were trapped. Notice that as the percentage of inert substances
becomes greater, the swelling and the vacuole size diminishes. This tends to show
that inert addition either allows the gases to exit through the viscous mass or
the viscosity of the fluid vitrinoid Type VII has been lowered to allow normal
bubbling off of the gases. Figure 22 again shows a distinctive dilution strength-
yield in which over 50% dilution is necessary before the strength is increased
approximately 20% over that of the pure maceral. Note the wide range of strength
beneficiation.

Vitrinoid Type VIII differs from all other vitrinoid types. Note the frothiness
of the buttons (Figure 23) and the projections on the button tops. The frothiness
is apparently due to fast coking in which the gases of the mass were trapped in the
cell structure. The top projections indicate that the outer button wall was coked
and solidified quickly forcing the inner fluid material to erupt through the top
of the button. Greater than 50% of inert material can be incorporated into the mass
and structure stabilization is brought about by the addition of inert material. The
button cross-sections (Figure 24) show that dilution with inert material initially
increases swelling and central vacuole development. In effect inert dilution causes
the mass to become more viscous thus presenting a barrier to escaping gases. Figure
25 illustrates the strength-yield characteristics of vitrinoid Type VIII.

The tests dealing with the assimilation capacities of these macerals of coal led to many important conclusions. The first and most obvious is that each entity tested displays a differing behavior pattern. Figure 26 compares the two type extremes showing their apparent assimilation potentials. Figure 27 compares five types of vitrinoid by illustrating the button produced by the pure vitrinoid types and the blend of that type with inert material that produced the highest strength. In Figure 28, coke button cross-sections show the structure and vacuole development of the pure materials, and in this figure the blends yielding the highest strength coke and the maximum vacuole development are also depicted.

This research has produced data that shows graphically that these materials differ in at least optical, physical and thermal properties. The data presented here has all been slanted toward establishing the basis for evaluating bituminous coal for use in metallurgical coke production. However, this is not the only application that will come from this type of study. Work is nearing completion on the effect of the vitrinoids on one another. It is important to know the affects of one entity on the other because a coal seam generally has one predominant vitrinoid type and two or three others that occur in quantities large enough to effect the commercial products. Once the critical data are obtained it should be possible to describe the combustion, carbonization, and hydrogenation potential of a coal seam from small samples such as those obtained in exploratory drilling operations. In addition, such information should provide the basis for prescribing more efficient preparation and blending operations. Through these avenues a contribution should be made to increasing the efficiency and effectiveness with which coal is utilized.

References

Spackman, W., 1958. The maceral concept and the study of modern environemtns as a means of understanding the nature of coal, Trans. New York Acad. Sci. 20: 411-423.

Spackman, W., Brisse, A.H., and Berry, W.F., 1957. Basic coal composition and its relationship to preparation and carbonization, Preprints A.I.M.E. Annual Meetings, New Orleans.

Stopes, M.C., 1935. One the petrology of banded bituminous coal, Fuel 14:4-13.

COKE STRENGTH
(MICROSTRENGTH)

RELATIONSHIP OF VITRINITE CONTENT
TO
COKE STRENGTH

Figure 2

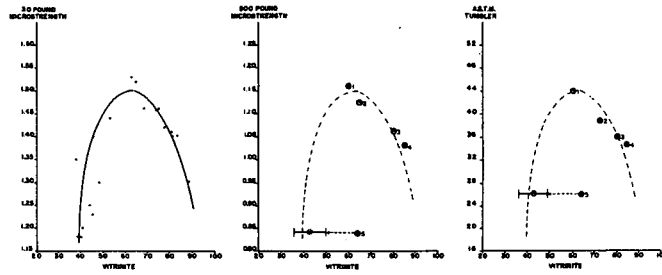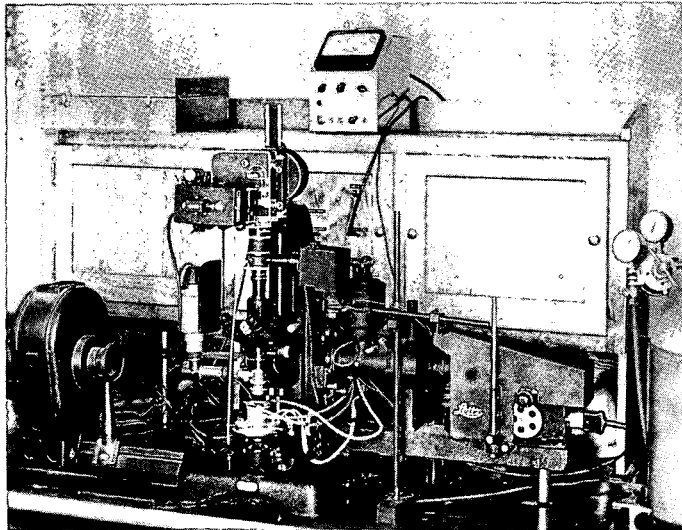MICROSCOPIC PETROGRAPHIC ANALYSIS
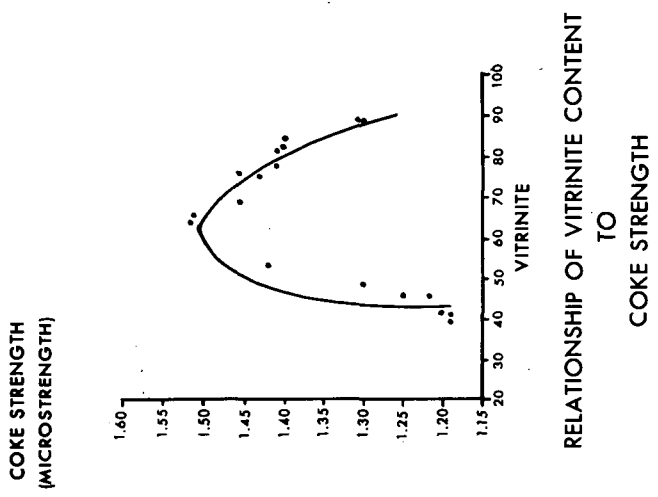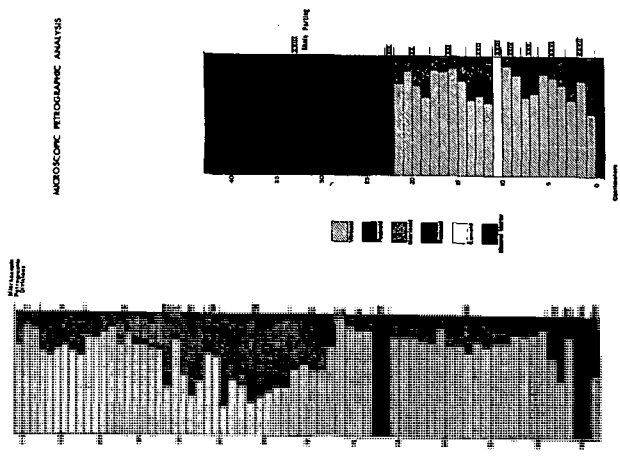
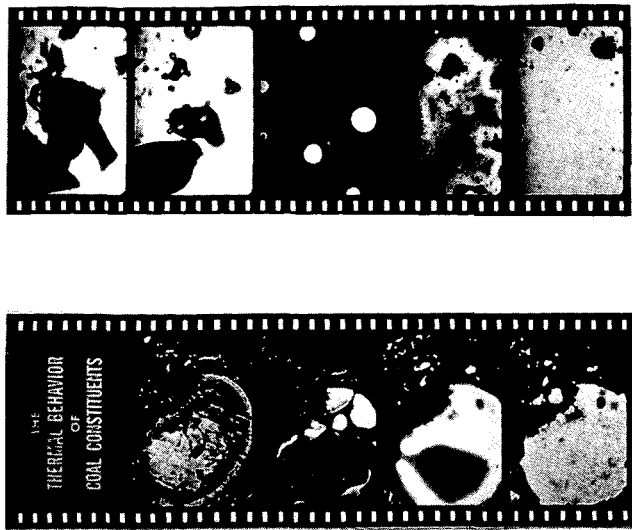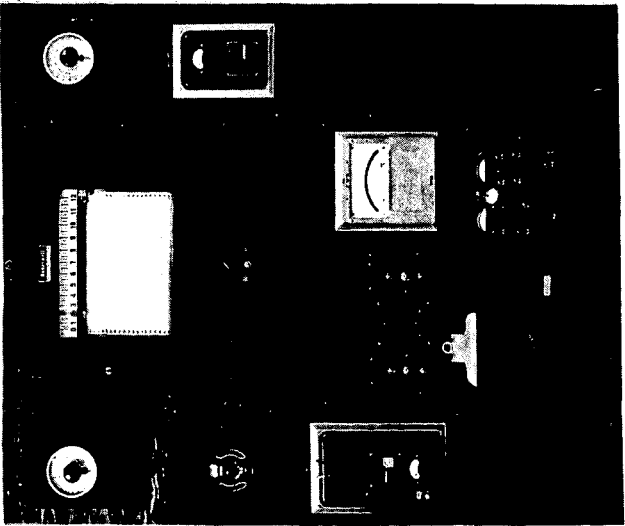Figure 1

Figure 3

Figure 4

Figure 6

Figure 5

THERMOPLASTIC PROPERTIES
OF
VITRINOIDS AND RELATED SUBSTANCES
(3 C./min.)

		Average Fluid Range (C.)	Average Softening Point (C.)	Average Solidification Point (C.)	Capacity to Fuse with Similar Particles
NON-PLASTIC	TYPE I	None	None	None	None
	TYPE II	None	None	None	None
SEMI-PLASTIC	TYPE IX	Semisolid	453	552	None
P L A S T I C	TYPE VIII	75	420	495	Fair
	TYPE V	109	411	520	Good
	TYPE VI	125	426	551	Fair
	TYPE IV	161	409	571	Good
	TYPE III	161	412	573	Poor
	TYPE VII	182	416	598	Poor

Figure 7

THERMOPLASTIC PROPERTIES
OF
VITRINOIDS AND RELATED SUBSTANCES
(12 C. min.)

		Average Fluid Range (C.)	Average Softening Point (C.)	Average Solidification Point (C.)	Capacity to Fuse with Similar Particles
NON-PLASTIC	TYPE I	83	417	500	Poor
	TYPE II	95	412	507	Good
SEMI-PLASTIC	TYPE IX	Semisolid	440	550	Poor
P L A S T I C	TYPE V	110	416	526	Excellent
	TYPE VI	124	431	555	Excellent
	TYPE IV	165	406	571	Excellent
	TYPE III	164	407	571	Good
	TYPE VIII	203	447	650	Good
	TYPE VII	220	411	631	Fair

Figure 8

EFFECT OF SHOCK HEATING

on

VITRINOIDS II AND VII
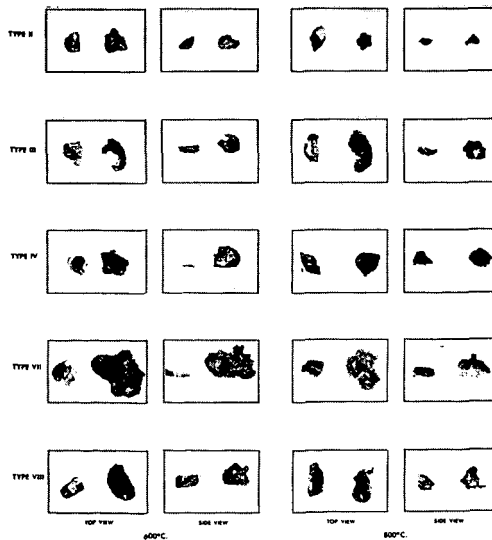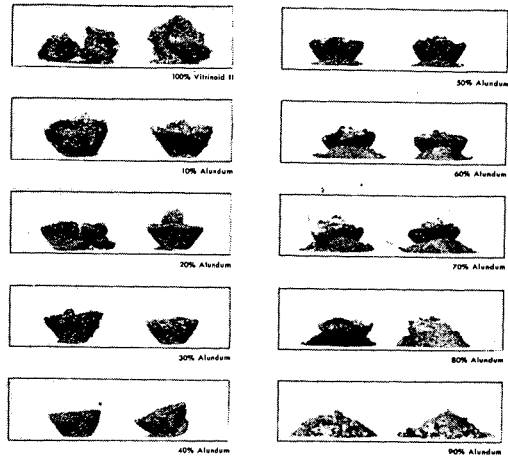
Figure 9

Figure 10

EFFECT OF INERT MATERIAL ON COKE PRODUCED FROM VITRINOID TYPE II

Figure 11

EFFECT OF BLENDING INERT MATERIAL
WITH VITRINOID TYPE II

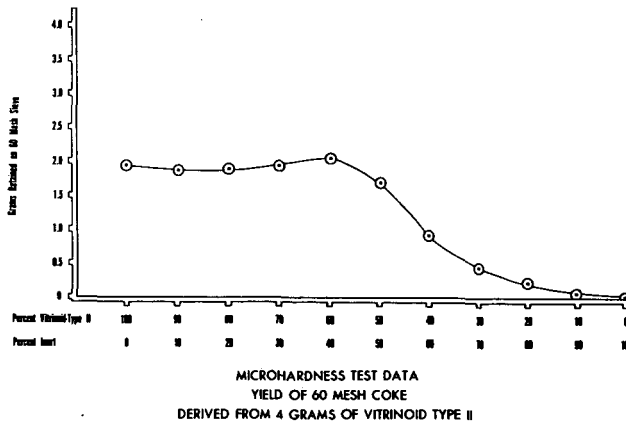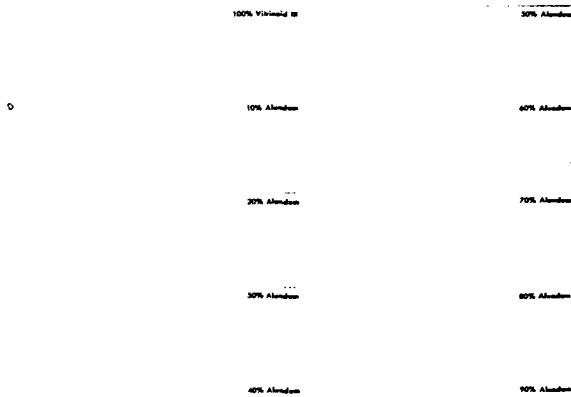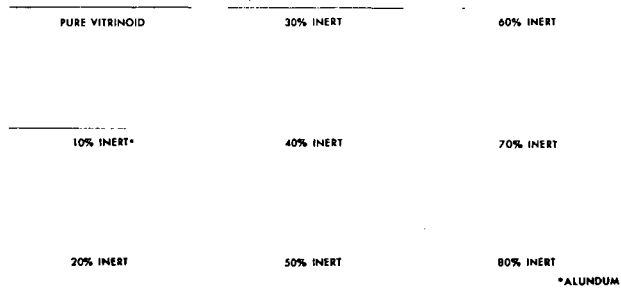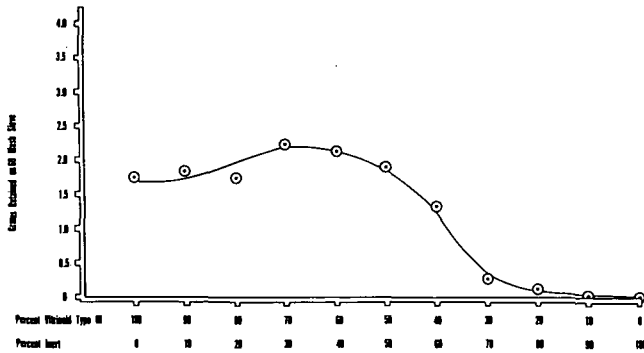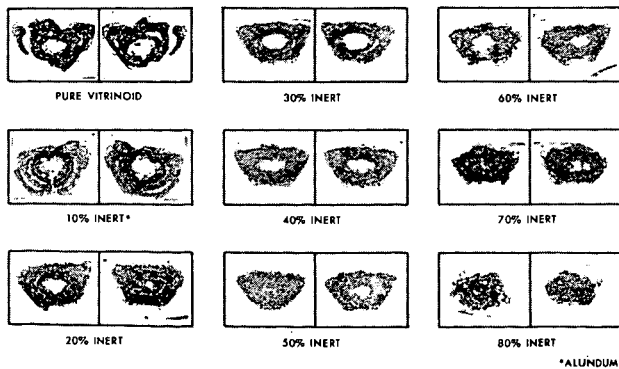PURE VITRINOID   30% INERT   60% INERT

10% INERT*   40% INERT   70% INERT

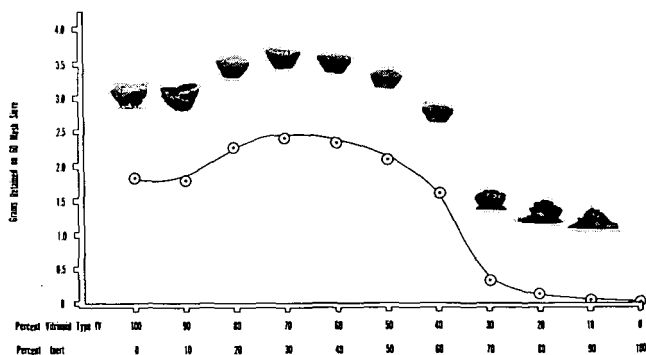20% INERT   50% INERT   80% INERT

*ALUNDUM

Figure 12

MICROHARDNESS TEST DATA
YIELD OF 60 MESH COKE
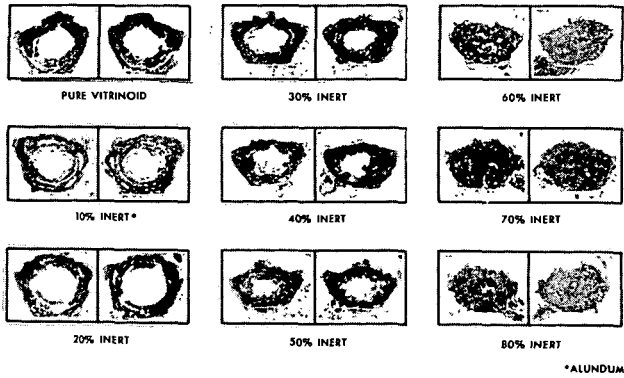DERIVED FROM 4 GRAMS OF VITRINOID TYPE II
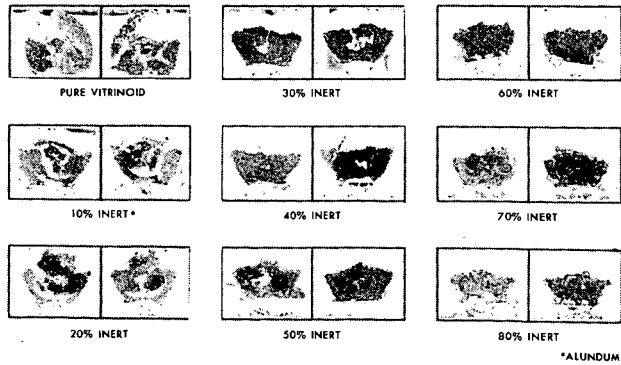
Figure 13

EFFECT OF INERT MATERIAL ON COKE PRODUCED FROM VITRINOID TYPE III

Figure 14

EFFECT OF BLENDING INERT MATERIAL
WITH VITRINOID TYPE III

PURE VITRINOID	30% INERT	60% INERT
10% INERT*	40% INERT	70% INERT
20% INERT	50% INERT	80% INERT
		*ALUNDUM

Figure 15

MICROHARDNESS TEST DATA
YIELD OF 60 MESH COKE
DERIVED FROM 4 GRAMS OF VITRINOID TYPE III

Figure 16
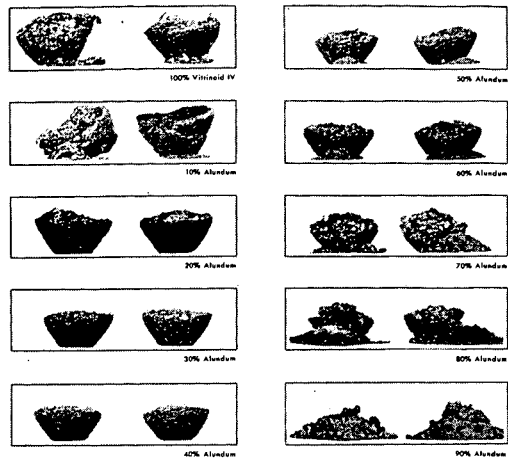
EFFECT OF INERT MATERIAL ON COKE PRODUCED FROM VITRINOID TYPE IV

Figure 17

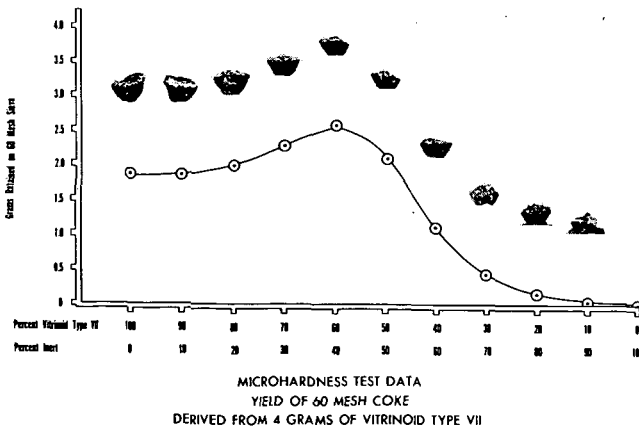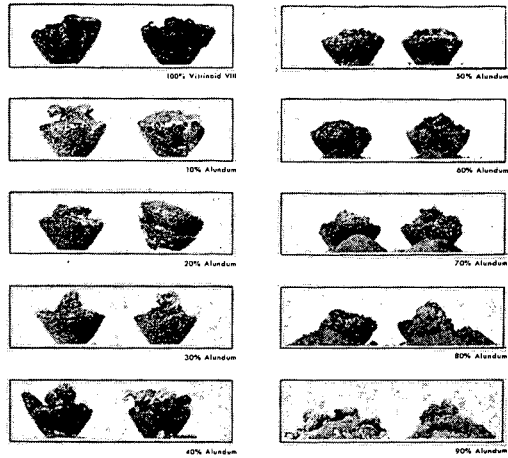EFFECT OF BLENDING INERT MATERIAL
WITH VITRINOID TYPE IV

PURE VITRINOID | 30% INERT | 60% INERT
10% INERT* | 40% INERT | 70% INERT
20% INERT | 50% INERT | 80% INERT

*ALUNDUM

Figure 18

MICROHARDNESS TEST DATA
YIELD OF 60 MESH COKE
DERIVED FROM 4 GRAMS OF VITRINOID TYPE IV

Figure 19
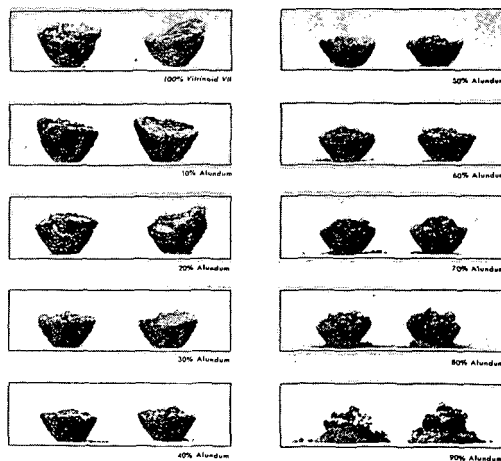
EFFECT OF INERT MATERIAL ON COKE PRODUCED FROM VITRINOID TYPE VII

Figure 20

EFFECT OF BLENDING INERT MATERIAL
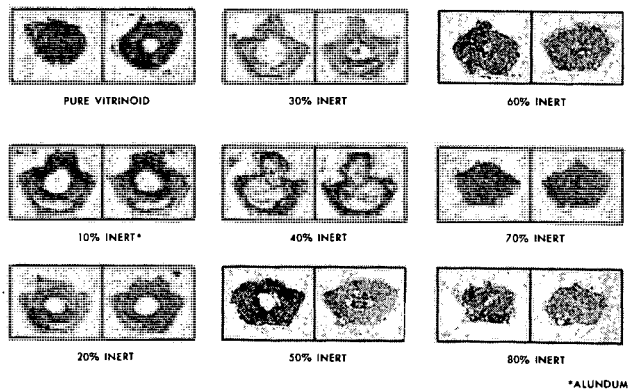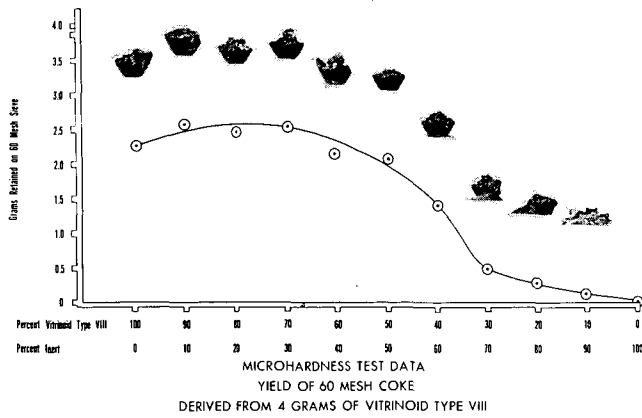## WITH VITRINOID TYPE VII

PURE VITRINOID   30% INERT   60% INERT

10% INERT*   40% INERT   70% INERT

20% INERT   50% INERT   80% INERT

*ALUNDUM

Figure 21

MICROHARDNESS TEST DATA
YIELD OF 60 MESH COKE
DERIVED FROM 4 GRAMS OF VITRINOID TYPE VII

Figure 22

EFFECT OF INERT MATERIAL ON COKE PRODUCED FROM VITRINOID TYPE VIII

Figure 23

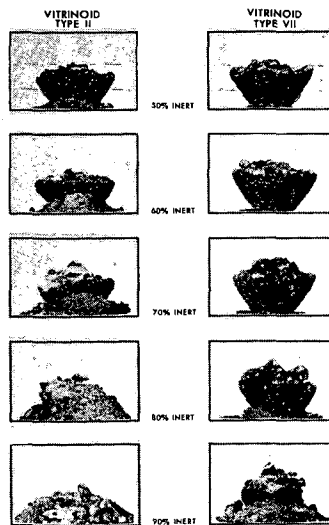EFFECT OF BLENDING INERT MATERIAL
WITH VITRINOID TYPE VIII

*ALUNDUM

Figure 24

MICROHARDNESS TEST DATA
YIELD OF 60 MESH COKE
DERIVED FROM 4 GRAMS OF VITRINOID TYPE VIII

Figure 25
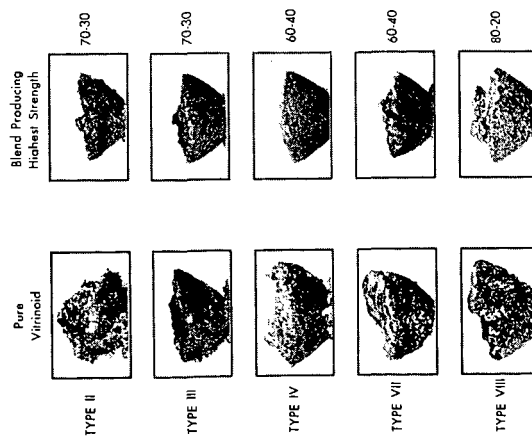

COMPARISON
of
INERT ASSIMILATING CAPACITIES

Figure 26

INFLUENCE OF VITRINOID TYPES ON COKE STRUCTURE

Figure 28

COMPARISON OF COKE
DERIVED FROM PURE VITRINOIDS
WITH COKE PRODUCED FROM BEST BLEND

Figure 27